

“A Preliminary Investigation of the Conditions which determine the Stability of Irreversible Hydrosols.” By W. B. HARDY, Fellow of Gonville and Caius College, Cambridge. Communicated by F. H. NEVILLE, F.R.S. Received January 12,—Read January 25, 1900.

It has long been held that a large number of colloidal solutions are related to or identical with suspensions of solid matter in a fluid in which the particles of solid are so small as to settle at an infinitely slow rate. Such solutions are the colloidal solutions of metals and of sulphides such as those of antimony, arsenic, and cadmium. Such solutions belong to the class of irreversible colloidal mixtures. A rise of temperature assists the process of coagulation or precipitation;* but neither a further rise nor a fall of temperature will cause the reformation of the hydrosol. On this ground they may provisionally be classed with such colloidal solutions as those of silica, ferric hydrate, alumina, &c., and with the modification of the albumen of white of egg which is produced by heating an aqueous solution to the boiling point. I also add to the class, for reasons to be developed in the following pages, the suspension of mastic in water which is produced by adding a dilute alcoholic solution of the gum to water.

Looked at from the point of view of the phase rule, the equilibrium in these hydrosols, if they really consist of minute solid particles dispersed in a fluid, is not necessarily between the solid particle and water, but between the solid particle and a solution of the particular solid in water. The hydrosol of gum mastic gives off a vapour of the gum of a density sufficient to affect the olfactory organs, and, therefore, the water must contain a definite quantity in solution. Similarly, as it is probable that no substance is completely insoluble, we may assume that in all the examples a portion of the solid is in true solution in the fluid. As the solid which is not in true solution is dispersed in particles whose diameter is, as a rule, very much smaller than the mean wave length of light, it follows that the surface of contact between solid and fluid is very great for unit mass of the former. The opportunity for evaporation and condensation of the solid matter of the particles afforded by the immense surface of contact is so very great that, although only an immeasurably minute quantity of the solid may be in true solution at any one time, this quantity, minute though it be, is probably an important factor in determining the equilibrium between solid and fluid.

* Elsewhere (*Journal of Physiology*, vol. 24, 1899, p. 172) I have shown that precipitation and coagulation are not discontinuous processes. Coagulation gives way to precipitation when the concentration of the solid phase falls below a certain amount.

It is necessary to keep such considerations as these in mind in view of the readiness with which these mixtures have been regarded as simple suspensions* in which the only relation between solid and fluid is a mechanical one. These hydrosols are, as a matter of fact, singularly stable when pure. They can, for instance, be concentrated by boiling to a remarkable extent, and their stability depends upon complex relations between fluid and solid, which gives the former, so to speak, a definite hold over the latter.

Mode of Preparation of the Different Solutions.—The hydrosol of gold was prepared by adding a couple of drops of a solution of phosphorus in ether to about a litre of a very dilute solution of gold chloride. The fine ruby-coloured fluid which was formed was dialysed against distilled water† for fourteen days, and then concentrated by boiling. The hydrosol of silicic acid was prepared by acting on soluble glass with excess of hydrochloric acid, and dialysing the product. A hydrosol of ferric hydrate was prepared by prolonged dialysis of the solution in ferric chloride.

The hydrosol of gum mastic was prepared by adding a very dilute solution of the gum in alcohol to distilled water. It was dialysed for fourteen days against distilled water. The hydrosol of heat-modified egg-white was prepared by dissolving white of egg in nine times its volume of distilled water, filtering and boiling. The result should be a brilliant fluid which scatters blue light. Surface action, however, plays an extraordinary part. If the solution is boiled in a test-tube a milky fluid is formed and a film of proteid is left on the glass; a second quantity boiled in the same test-tube comes out less milky, until, when the proteid film is sufficiently thick to eliminate all action by the glass, the solution after boiling contains the proteid dispersed as particles so small that they scatter pure blue light. After preparation the hydrosol was dialysed against distilled water for some days.

Behaviour of the Hydrosols in an Electric Field.—It has long been known that the particles in these colloidal solutions move in an electric field. Zgismondy‡ found that the gold in colloidal solutions moves against the current. Picton and Linder§ established the important fact that the direction of movement of the particles, as compared with the direction of the current, depends upon their chemical nature. I have shown that the heat-modified proteid is remarkable in that its direction of movement is determined by the reaction acid, or alkaline of the fluid

* Cf., for instance, Stoeckl and Vanino, 'Zeits. f. phys. Chem.,' vol. 30, 1899, p. 98; also Ostwald, 'Lehrbuch.'

† In working with these colloidal solutions it is very necessary to use distilled water freed from dissolved carbonic acid.

‡ 'Lieb. Ann.,' vol. 301, p. 29.

§ 'Journal of Chem. Soc.,' vol. 70, 1897, p. 568.

in which it is suspended.* An immeasurably minute amount of free alkali causes the proteid particles to move against the stream, while in presence of an equally minute amount of free acid the particles move with the stream. In the one case, therefore, the particles are electro-negative, in the other they are electro-positive.

Since one can take a hydrosol in which the particles are electro-negative and, by the addition of free acid, decrease their negativity, and ultimately make them electro-positive, it is clear that there exists some point at which the particles and the fluid in which they are immersed are iso-electric.

This iso-electric point is found to be one of great importance. As it is neared, the stability of the hydrosol diminishes until, at the iso-electric point, it vanishes, and coagulation or precipitation occurs, the one or the other according to whether the concentration of the proteid is high or low, and whether the iso-electric point is reached slowly or quickly, and without or with mechanical agitation.

This conclusion can be verified experimentally in many ways. If a coagulum or precipitate of the proteid particles made either by the addition of a neutral salt, or by the addition of acid or alkalis, be thoroughly washed, made into a fine mud in an agate mortar, and suspended in water in a U-tube, it rapidly subsides. The establishment of an electric field having a potential gradient of 100 volts in 10 cm. has no influence on the level of water or precipitate in forty-eight hours. If, now, the smallest possible amount of caustic soda or acetic acid be added, the proteid will commence to move, so that in twenty hours the precipitate will rise in one or other limb until it nearly touches the platinum electrode.

Speaking generally, the hydrosol of ferric hydrate is stable only in the absence of free acids or alkalis or neutral salts. The hydrosol of heat-modified proteid is stable only in presence of free acid or alkali. The hydrosol of gum mastic is readily precipitated by acids, but is stable in presence of any concentration of monovalent alkalis. The general conditions of stability of these various hydrosols, therefore, are very different, yet they agree in manifesting the same important relation between the isoelectric point and the point of precipitation as is shown by the hydrosol of proteid.

In the hydrosol of ferric hydrate the particles are markedly electro-positive. A dilute hydrosol is coagulated by citric acid when the concentration of the latter reaches 1 gramme-molecule in 4,000,000 c.c. No matter how small the concentration of the ferric hydrate, the hydrosol becomes cloudy and settles. The rate of settling is, however, slow, being about 1 cm. an hour. In an electric field, having the form of a U-tube, the particles always settle slightly faster from the negative

* "The Coagulation of Proteid by Electricity," W. B. Hardy, 'Journal of Physiology,' vol. 24, 1899, p. 288.

electrode—the acceleration due to the electric field being about 5 mm. an hour. The suspended particles of ferric hydrate show, therefore, an exceedingly slight movement in a direction *opposite* to that which they manifest when in colloidal solution. In the latter condition they are markedly electro-positive; in the former they are exceedingly faintly electro-negative. An exceedingly faint electro-negative character is also conferred upon the ferric hydrate when the hydrosol is coagulated by ammonia, 1 gramme-molecule of the latter being present in 100,000 c.c.

If a fresh gel of silica is broken up in distilled water and carefully washed to free it from still uncoagulated silica, and from impurities, it is completely iso-electric with the water. It becomes markedly electro-negative, however, on the addition of the minutest trace of free alkali.

Gum mastic precipitated from a dilute hydrosol by adding barium chloride until the concentration is 1 gramme-molecule in 600,000 cm. is found to be iso-electric with the fluid. It is markedly electro-negative when in colloidal solution.

Picton and Linder have shown that the particles in these hydrosols gradually grow in size as the coagulation or precipitation point is neared.* It might, therefore, be urged that, as the movement of the particles in the electric field is, on Quincke's theory of electric endosmose, due to surface action, the fact that they do not move when in simple suspension as opposed to colloidal solution may be due to the diminution of the impelling force acting on a given volume.† This is, however, negated by the character of the experiments. The addition of a minute amount of free alkali to a mass of particles of coagulated silica which have settled to form a "mud" cannot alter the size of these relatively very large masses to any appreciable extent. And since in the case of ferric hydrate and proteid, the sign of the charge which the particles carry in the electric field is different on each side of the actual point of precipitation, that point must of necessity be an iso-electric point.

If the stability of the hydrosol is dependent upon a difference in electrical potential between the solid particles and the fluid, then one would expect that for, at any rate a short distance from the iso-electric point, the stability would vary simultaneously with the variation in the difference of potential. The experimental investigation of this question is beset by many difficulties. At present I know of no way of approaching the iso-electric point other than by the addition of salts,

* 'Journ. of Chem. Soc.,' vol. 61, 1892, p. 148.

† As a matter of fact, Lamb finds that the velocity of a particle is independent of its size or shape, provided that its dimensions are large compared with the slip, so perhaps the objection scarcely needs discussion. Lamb, 'Brit. Assoc. Report,' 1887, p. 502.

acids, or alkalis. One may, therefore, approach the point by the addition of, say, acid or alkali, and use a salt to measure the stability of the system, as in the experiment described later. In such experiments, however, the colloid particles are immersed in a complicated system of three components, the conditions of equilibrium of which cannot be arrived at from existing data. The conditions could be simplified by using, say, KHO or H_2SO_4 to approach the iso-electric point, and K_2SO_4 as a measure of the change of stability. A series of determinations with different systems of this kind may afford the requisite measurements.

A direct and conclusive proof that stability does decrease as the iso-electric point is approached was however obtained in two ways. The iso-electric point can be approached in the case of the hydrosol of proteid by the withdrawal of either the free acid or the free alkali, as the case may be. As it is neared, the proteid particles increase in size, so that instead of scattering blue light, they scatter white light; thus the surface of contact of fluid and solid gradually diminishes as the point is neared. The second experiment, though not a quantitative one, is very convincing. A hydrosol of gum mastic dialysed as pure as possible is not destroyed by mechanical agitation even when long continued. If, however, a salt is added in an amount so small that it just fails to coagulate the hydrosol, the latter is rendered so unstable that it is destroyed by shaking.

Experiments were made to determine whether the particles actually carry a charge. An electric field which was practically uniform was made by using flat electrodes of the same size, which were placed parallel to one another at the ends of a straight tube. The particles were found to move in all parts of the field; they therefore carry a definite charge which, according to Quincke's theory of the movement of particles in an electric field, would be a surface charge, each particle being surrounded by a double layer of electricity.

Action of Salts.—The power possessed by salts of destroying colloidal solutions was noticed by Graham. The subject was, however, first accurately investigated by H. Schulze.* He showed that the power which various salts possess of precipitating a hydrosol of sulphide of arsenic is related to the valency of the metal, while the valency of the acid has little influence. The increase in the precipitating or coagulating power produced by increase in valency is very great. If coagulative power be defined as the inverse of the concentration in gramme-molecules per litre necessary to convert a given hydrosol into a hydrogel, then from Schulze's measurements the coagulative power of metals of different valency is:—

$$\text{R}' : \text{R}'' : \text{R}''' = 1 : 30 : 1650.$$

* 'Journ. f. prakt. Chemie,' vol. 25, 1882, p. 431.

Schulze's conclusions were verified by Prost,* who used sulphide of cadmium, and Picton and Linder, who used the sulphide of antimony.† The last-named workers added the important fact that a small portion of the coagulating salt is decomposed, the metal being entangled in the coagulum.

The measurements which I have made with various colloidal solutions both confirm Schulze's results, and bring out a new relation, which may be stated as follows:—

The coagulative power of a salt is determined by the valency of one of its ions. This prepotent ion is either the negative or the positive ion, according to whether the colloidal particles move down or up the potential gradient. The coagulating ion is always of the opposite electrical sign to the particle.

The salts employed to determine this point were the sulphates of aluminium, copper, magnesium, potassium, and sodium; the chlorides of copper, barium, calcium and sodium, and the nitrate of cadmium. Solutions containing 1 gramme-molecule in 2000 c.c. were prepared.

The experiments may be summarised as follows:—

Silica dialysed free from Chlorides, Electro-negative.

Concentration of Coagulating Salt 1 gramme-mol. in 120,000 c.c.
Temperature 16°.

| Coagulated at once. | In 10 mins. | In 2 hours. | In 24 hours. | Still fluid. |
|------------------------------|----------------------------|-----------------|--------------------------|---------------|
| $\text{Al}_2(\text{SO}_4)_3$ | CuSO_4 | MgSO_4 | K_2SO_4 | NaCl |
| | CuCl_2 | | Na_2SO_4 | Control. |
| | $\text{Cd}(\text{NO}_3)_2$ | | | |
| | BaCl_2 | | | |

This illustrates many experiments.

Proteid in presence of trace of Alkali, Electro-negative.

Temperature 16°. Coagulating Salt 1 gramme-mol. in 80,000 c.c.

| Coagulated at once. | On slightly warming. | Did not coagulate. |
|------------------------------|----------------------|--------------------------|
| $\text{Al}_2(\text{SO}_4)_3$ | MgSO_4 | Na_2SO_4 |
| $\text{Cd}(\text{NO}_3)_2$ | BaCl_2 | K_2SO_4 |
| CuSO_4 | CaCl_2 | NaCl |
| CuCl_2 | | |

Proteid in presence of trace of Acetic Acid, Electro-positive.

| Coagulated instantly. | No effect. |
|--------------------------|----------------------------|
| Al_2SO_4 | CuCl_2 |
| CuSO_4 | $\text{Cd}(\text{NO}_3)_2$ |
| K_2SO_4 | BaCl_2 |
| Na_2SO_4 | NaCl |
| MgSO_4 | |

* 'Bull. de l'Acad. Roy. de Sci. de Belg.,' ser. 3, vol. 14, 1887, p. 312.

† 'Journ. Chem. Soc.,' vol. 67, 1895, p. 63.

Mastic, Dialysed, Neutral, Electro-negative.

Temperature 16°. Concentration of Coagulating Salts, 1 gramme-mol. in 50,000.

| Coagulates at once. | No coagulation. |
|------------------------------|--------------------------|
| $\text{Al}_2(\text{SO}_4)_3$ | K_2SO_4 |
| CuSO_4 | Na_2SO_4 |
| CuCl_2 | NaCl |
| $\text{Cd}(\text{NO}_3)_2$ | |
| MgSO_4 | |
| BaCl_2 | |

Ferric Hydrate, Dialysed, Neutral, Electro-positive.

Temperature 16°. Coagulating Salt 1 gramme-mol. in 100,000.

| Coagulates at once. | Does not coagulate. |
|------------------------------|----------------------------|
| $\text{Al}_2(\text{SO}_4)_3$ | CuCl_2 |
| CuSO_4 | $\text{Cd}(\text{NO}_3)_2$ |
| MgSO_4 | NaCl |
| K_2SO_4 | BaCl_2 |
| Na_2SO_4 | |

Gold, Dialysed for fourteen days against Distilled Water, very faintly Acid. Electro-negative.

Temperature 16°. Coagulating Salt 1 gramme-mol. in 200,000.

| Red changes to blue* instantly in— | No change. |
|---------------------------------------|--------------------------|
| $\text{Al}_2(\text{SO}_4)_3$ | NaCl |
| CuSO_4 | Na_2SO_4 |
| CuCl_2 | K_2SO_4 |
| $\text{Cd}(\text{NO}_3)_2$ | |
| MgSO_4 | |
| BaCl_2 | |

Only one comment on these experiments is needed. Solutions of $\text{Al}_2(\text{SO}_4)_3$, $\text{Cd}(\text{NO}_3)_2$, CuCl_2 , and CuSO_4 , are acid to litmus, while MgSO_4 , and BaCl_2 are neutral to litmus, but acid to phenol phthalein. This acidity has a disturbing action in some cases—the system acts not only as a neutral salt, but also as a free acid. Thus the hydrosol of proteid when brought very near to the point of precipitation by dialysis is more sensitive to the more acid than to the less acid salts of the bivalent metals. The effect of the acid or basic reaction of the

* The relation of the colours of hydrosols of gold to the size of the particles has been investigated by Stoeckl and Vanino ('Zeits. f. phys. Chem.,' vol. 30, 1899, p. 98). The change from red to blue indicates an increase in the size of the particles.

salt on the hydrosol is as a rule small compared with the effect of the metal ion. Thus the stability of a hydrosol of electro-positive proteid is increased by free acid, yet the acid salts find their proper place in the scale of valency. Again, ferric hydrate is coagulated by nitric acid when the concentration reaches 1 gramme-mol. in 2500 c.c.; yet the cadmium salt of this acid is not much more potent than the "neutral" salts MgSO_4 , BaCl_2 .

Temperature 16°. Concentration necessary to Coagulate Ferric Hydrate.

| Salt. | | | |
|--------------------------------|------------------|----------------|---|
| K_2SO_4 | 1 gramme-mol. in | 4,000,000 c.c. | |
| MgSO_4 | " " | 4,000,000 | " |
| BaCl_2 | " " | 10,000 | " |
| NaCl | " " | 30,000 | " |
| $\text{Cd}(\text{NO}_3)_2$... | " " | 50,000 | " |

The extraordinary rise in coagulative power with an increase in valency, which was observed by Schulze, Prost, and Picton and Linder, holds in all cases. In order to measure it for ferric hydrate, I used Schulze's method, in which a drop of the hydrosol is allowed to fall into a large volume of the solution of the salt. A number of experiments were made until the concentration of the salt was found which just sufficed to coagulate the drop. In the case of gold and mastic the process was reversed, the salt solution being added drop by drop to a measured quantity of the hydrosol. I append the results :—

Gum Mastic, Neutral. Temperature 40°.

| | | | |
|-------------------------------|------------------|-------------|---|
| BaCl_2 | 1 gramme-mol. in | 86,000 c.c. | |
| NaCl | " " | 8,000 | " |
| MgSO_4 | " " | 68,000 | " |
| K_2SO_4 | " " | 8,000 | " |

Gold, very faintly acid. Temperature 16°.

| | | | |
|-------------------------------|------------------|-------------|---|
| NaCl | 1 gramme-mol. in | 72,000 c.c. | |
| BaCl_2 | " " | 500,000 | " |
| K_2SO_4 | " " | 75,000 | " |

The figures for ferric hydrate have already been given. It has been pointed out that if specific molecular coagulative power be defined as the inverse of the volume occupied by one gramme-molecule of a substance when it just suffices to bring about coagulation, then this value (K) varies with the valency of the active ion approximately according to the square and cube :—

$$R' : R'' : R''' = K : K^2 : K^3.$$

The relation really is not as simple as this; it is complicated by the change which the specific molecular conductivity of a salt undergoes with change in concentration. The theoretical considerations have been dealt with elsewhere.* For convenience of description, however, I will call this relation the relation of the square and cube.

Action of Acids and Alkalis.—The values for K furnished by these substances show relations to valency even more interesting than that found with salts. As in the case of salts, their action is entirely dependent upon the electric properties of the colloid particles.

When the colloid particles are electro-negative, alkalis either do not cause precipitation at any concentration, or if they do cause precipitation the value of K does not vary in any simple way with variations in valency.

When the particles are electro-positive, K increases with valency, but the relation of the square and cube does not hold. Instead, one finds that K varies directly with the chemical activity of the solution.

Acids have the reverse relations. When the particles are electro-negative, the value of K varies directly with the chemical activity of the solution; while if these particles are electro-positive, acids either have no precipitating power, or if K has any value, then (in the particular case measured) the value varies with valency according to the square and cube.

The various measurements are brought together in the following table. The specific conductivities were calculated from the British Association tables.†

* Hardy and Whetham, 'Journal of Physiology,' vol. 24, 1899, p. 288, and Whetham, 'Phil. Mag.,' November, 1899.

† "The Electro-chemical Properties of Aqueous Solutions." T. C. Fitzpatrick 'Brit. Assoc. Report,' 1893.

Coagulating Solution.

| Hydrosol. | Concentration necessary to produce coagulation. | | Specific conductivity of coagulating solution at $18^{\circ} \times 10^{12}$. | Temperature. |
|---------------------------|---|--------------------------|--|--------------|
| | 1 gramme-mol. in c.c. = | Gramme equiv. per litre. | | |
| Mastic, electro-negative. | Ammonia... | ∞ | .. | 16-100° |
| | KaOH | ∞ | .. | 16-100 |
| | KOH | ∞ | .. | 16-100 |
| | Ba(OH) ₂ ... | 0.048 | 100 | 16 |
| | H ₃ PO ₄ | 0.015 | 13.9 | 17 |
| | Acetic acid. | 0.7 | 12.6 | 17 |
| | HCl | 0.004 | 14.5 | 17 |
| | HNO ₃ | 0.004 | 14.3 | 17 |
| | H ₂ SO ₄ | 0.004 | 13.2 | 17 |
| | Oxalic acid.. | 0.009 | 14.4 | 17 |
| | BaCl ₂ | 0.022 | [20] | 40 |
| | MgSO ₄ | 0.028 | [18] | 40 |
| | NaCl | 0.12 | [110] | 40 |
| | K ₂ SO ₄ | 0.24 | [250] | 40 |
| | Ammonia... | ∞ | .. | 17-100 |
| Gold, electro-negative. | NaOH | 0.08 | 152 | 17 |
| | KOH | 0.09 | 189 | 17 |
| | Ba(OH) ₂ ... | 0.16 | .. | 100 |
| | | | | |

The values for specific conductivity are given for a temperature different from that of observation, but they serve to show the general relation.

Solution saturated at 17° has no action.

Coagulating Solution—*continued*.

| Hydrosol. | Concentration necessary to produce coagulation. | | Specific conductivity of coagulating solution at $18^{\circ} \times 10^{13}$. | Temperature. | |
|---|---|--------------------------------|--|--------------|---|
| | 1 gramme- mol. in c.c. = | Gramme equiv. per litre. | | | |
| Ferric hydrate, electro- positive. | Ca(OH) ₂ ... | .. | .. | 17° | No action when saturated. |
| | HCl | 123,000 | 0.008 | 17 | |
| | H ₂ SO ₄ | 238,544 | 0.0084 | 17 | |
| | NaC | 72,000 | 0.013 | 17 | |
| | BaCl ₂ | 500,000 | 0.004 | 17 | |
| | K ₂ SO ₄ | 75,000 | 0.026 | 17 | |
| | KHO | 1,000,000 | 0.001 | 16 | |
| | Ba(OH) ₂ ... | 2,000,000 | 0.001 | 16 | |
| | HCl | 1,800 | 0.5 | 16 | |
| | HNO ₃ | 2,000 | 0.5 | 16 | |
| | H ₂ SO ₄ | 1,000,000 | 0.002 | 16 | |
| | Oxalic acid . | 1,000,000 | 0.002 | 16 | |
| | Citric " | 4,000,000 | 0.0007 | 16 | |
| | K ₂ SO ₄ | 3,200,000 | 0.0006 | 16 | |
| | MgSO ₄ | 4,000,000 | 0.0005 | 16 | |
| | BaCl ₂ | 6,000 | 0.3 | 16 | |
| | NaCl | 20,000 | 0.5 | 16 | |
| | | | | | Specific conductivity by analogy with similar acids will not be greater than the value given. |

The figures in the fourth column are very remarkable. When the particles are electro-negative, equicoagulative solutions of acids agree in their electric conductivity within the limits of experimental error. The same relation is clearly shown if one takes the measurements which Picton and Linder made of the power possessed by acids of coagulating the hydrosol of arsenious sulphide.

| Acid. | Value of K referred to Al_2Cl_6 as unity. | Sp. mol. conductivity when 1 gr. equiv. = 1000 c.e. |
|-----------|--|--|
| HBr | 0.001 | 2950 |
| HI | | |
| HCl | | |
| HNO_3 | | |
| H_2SO_4 | 0.0006 | 1935 |
| Oxalic | 0.0005 | 578 |
| H_3PO_4 | 0.00007 | 230 |

When, however, the particles are electro-positive, the conductivity of equicoagulative strengths of acids varies to a remarkable extent.

| Acids. | H' | : | H'' | : | H''' |
|----------------------------------|------|---|------|---|------|
| Mastic, electro-negative | 12.6 | | 14.4 | | 13.9 |
| Ferric hydrate, electro-positive | 1650 | | 6.8 | | 0.7 |

Now specific conductivity (C) has the relation

$$C = n\alpha(u+v)$$

where α is the fraction of the total number of molecules (n) which are dissociated at any one moment, and $u + v$ is the sum of the velocities of the two ions. The factor $u + v$ plays an important part, as will be seen by comparing the values for $n\alpha$ in equicoagulative solutions of acids with slowly moving ions with those with rapidly moving ions:—

| | $n\alpha$. |
|-------------------|-------------|
| H_3PO_4 | 0.01 |
| Acetic acid | 0.07 |
| HCl | 0.004 |
| H_2SO_4 | |
| HNO_3 | |
| | |

This, however, is probably partly due to the fact that owing to the manner in which the coagulative power was measured, time has practically a constant small value. The values for n might, perhaps, be different if the duration of the experiments were prolonged indefinitely.

The important point, however, which calls for notice is that the function $\alpha(u + v)$ is a numerical measure of the chemical activity of the substance at a given concentration, so that we reach the important conclusion that *the concentration of acids necessary to coagulate electro-negative colloid particles, and of alkalis necessary to coagulate electro-positive particles, is determined by the laws which govern ordinary chemical equilibrium.*

In the case of the action of salts on these hydrosols, the relation is not so simple. K does not vary directly with $\alpha(u + v)$, but contains a factor which is approximately squared or cubed by a change from a mono-valent to di- or tri-valent ions. The relation can therefore be best expressed as

$$K = n\alpha(u + v)A^x$$

where x is positive and increases rapidly with an increase in the valency of the ion whose electric charge is of the opposite sign to that on the particles.

I should interpret these relations by the suggestion that in the former the acid or alkali alters the difference of potential at the surface of the particles by altering the character of the fluid, and in that way modifies the stability of the hydrosol; in the latter the active ions of the salt act directly upon the solid particles, or, perhaps, on the charge which these carry, and thus play a part which is, perhaps, generally similar to the action of ions when they furnish nuclei for the condensation of vapour. Picton and Linder have shown that the active ions are actually entangled in, and form part of, the coagulum.*

The former relation may profitably be placed beside Brühl's conclusions that the action exerted by a fluid upon the substance dissolved in it is determined by the chemical characters of the former, as well as of the latter. He has shown that the molecular refraction, the dielectric coefficient, and the power possessed by the fluid of dissociating or chemically changing the molecules of the substance dissolved in it are measured by the unsatisfied valency, or, to use another phrase, the residual energy of its molecules.

The action of acids or alkalis on a hydrosol, the particles of which are of the opposite electrical sign, seems to be compounded of these two actions. The acid or alkali may act as a salt, and exhibit the characteristic relation between K and the valency of the ion of the opposite electrical sign. An instance is furnished by the action of various acids on ferric hydrate, or the acid or alkali by *increasing* the difference of potential between the fluid and the solid particles may increase the stability of the hydrosol. This is markedly manifested by the increased stability given to the hydrosol of gum mastic by the addition of univalent alkalis. In the action of barium hydrate on this hydrosol, the segregating action of the metal ion overcomes the

* 'Journ. of the Chem. Soc.,' vol. 67, 1895, p. 63.

action exerted by the reagent in virtue of its alkalinity, the result is that the coagulative concentration of the alkali $\text{Ba}(\text{OH})_2$ gives a value for K which is less than that given by salts of bivalent metals, and the specific conductivity of the solution is of the same order as that of the coagulating concentration of salts of univalent metals. Against these suggestions, however, must be set the anomalous relations of the various alkalis to the hydrosol of gold.

Action of a Salt in presence of Varying Amounts of Acid or Alkali.

This was measured for one salt only, potassium sulphate, the colloidal solution being gold. The figures are as follows :—

Temperature 16°

| | Concentration 1 gr.-mol. in— c.c. | Concentration of the salt necessary to produce blue tint. 1 gr.-mol. K_2SO_4 in— c.c. |
|------------------|---|---|
| Acetic acid..... | 1,087 | 0 |
| | 16,000 | 324,000 |
| | 66,000 | 64,000 |
| | 330,000 | 50,000 |
| | (neutral*) | 28,500 |
| Ammonia | 113,333 | 10,000 |
| | 22,666 | 9,000 |
| | 4,900 | 20,000 |
| | 2,450 | 24,000 |
| | 980 | 20,000 |
| | 200 | Large amount of salt needed. |
| | 100 | Salt unable to act when saturated at 16° or at 100° . |

These results are shown in the curve. Ammonia alone will not aggregate the particles of gold. Up to a certain point, however, it decreases the stability of the system.

The conclusions can be summarised as follows :—The irreversible hydrosols which have been investigated are systems composed of solid particles dispersed through a solution of the substance of the solids in the water.

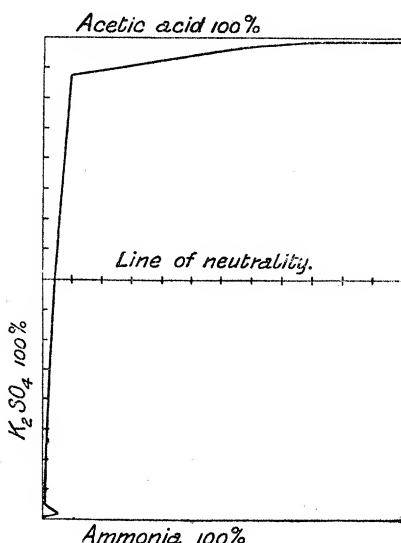
The stability of the system is related to the contact difference of potential which exists between the solid and the fluid phases, and which forms round each solid particle a double electrical layer. Such double electric layers round particles of any kind immersed in a fluid

* Except for a faint acid reaction of the gold solution, due probably to a trace of phosphoric acid.

would resist any movement of the particles through the fluid, because, as Dorn's experiments show, electric work is done in displacing the particles.* The effect would be the same as if the viscosity of the fluid was increased.†

The stability of the system may be destroyed by altering the difference of potential. Free acid, added to a hydrosol in which the particles are negative to pure water, will diminish the relative differ-

FIG. 1.



Action of potassium sulphate in presence of varying amounts of acetic acid or ammonia upon the hydrosol of gold. The abscissæ represent the volume of water which holds 1 gramme-molecule of the salt. The positive ordinates represent the reciprocals of the volume which holds 1 gramme-molecule of the acid, and the negative ordinates the reciprocals of the volume which holds 1 gramme-molecule of the alkali. Each division = 50,000 c.c.

ence of potential of the water. In this case the reagent acts directly on the water, and the coagulative activity of unit mass of the substance varies directly with its chemical activity when dissolved in water. The same relation seems to hold when free alkali is added to a hydrosol in which the particles are electro-positive.

The stability of the system may also be destroyed by induction, the active agents being free ions carrying a static charge.‡ In this case

* Wied. Ann., vol. 10, 1880, p. 70.

† This mode of stating the result I owe to Professor J. J. Thomson, and gladly acknowledge his kindness in discussing this and kindred points with me.

Whetham, *loc. cit.*

the action may be said to be on the particles, or rather on the electric layers immediately around them, and the active ions are those whose electric sign is the opposite of that of the charge on the surface of the particles. In this case coagulative power does not vary directly with variations in chemical activity. It rises exceedingly rapidly with a rise in the valency of the active ion, so that the relation

$$I' : I'' : I''' = n : n^2 : n^3$$

is approximately satisfied.

Picton and Linder have shown that when the concentration of the salt is insufficient to completely destroy the system, it is not wholly without action. A fresh point of equilibrium between solid and fluid is reached by an increase in the size of the particles and therefore a diminution in the extent and curvature of the surface of contact. The fact is of importance, because it introduces us to the possibility that the reagent may affect the size of the particles by altering the equilibrium between the part of the solid in solution and the part in suspension. Double electric layers round each particle are, according to Thomson, separated by a region of "uncompleted chemical combination" between the components.* The density of the field round the particles in hydrosols will therefore be a measure of the velocity of the solution and condensation between the particle and the liquid, and therefore the factor which determines whether the particles will on the whole grow, diminish, or remain stationary in size.

When acids or alkalis are added to hydrosols holding particles of the opposite electric sign to themselves, the simplest relation seems to be that univalent acids or alkalis increase the stability; bivalent acids or alkalis decrease it.

The view advanced in this paper implies that each particle in a hydrosol is surrounded by a zone in which the components are in a condition of chemical instability. According to Rayleigh,† such a zone is of finite thickness, and deep enough to contain several molecules. We therefore have in these hydrosols two phases, separated by a layer of extraordinarily large extent, which possesses considerable chemical energy. This, it seems to me, suggests an explanation of the catalytic powers so markedly manifested by hydrosols.

* 'Discharge of Electricity through Gases.' Scribner, 1898, p. 24.

† Thomson, *loc. cit.*, p. 26; Rayleigh, 'Phil. Mag.,' vol. 33, 1892, p. 468.